

# The kinetics and mechanism of the direct fluorination of polyethylenes

A P Kharitonov,<sup>1</sup> R Taege,<sup>2</sup> G Ferrier<sup>3</sup>  
and N P Piven<sup>1</sup>

1 Institute of Energy Problems of Chemical Physics (Branch) of the Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

2 Air Products GmbH, Fluorine Technology, 45523 Hattingen, Huettenstrasse 50, Germany

3 Air Products PLC, COE Packaged Gases, Weston Road, Crewe, Cheshire, CW1 6BT, United Kingdom

## Keywords

Direct fluorination, polyethylene, fluorinated layer, kinetics, mechanism

## Summaries

### The kinetics and mechanism of the direct fluorination of polyethylenes

Two types of low-density polyethylene (LDPE), five types of high-density polyethylene (HDPE), poly(vinyl fluoride) (PVF) and poly(vinylidene fluoride) (PVDF) were studied. The fluorination of LDPE and HDPE is a diffusion-controlled process and proceeds via a branched chain mechanism following an induction period. Initiation of the reaction takes place via the reaction of molecular fluorine with the C-H bond. The rate of fluorination of HDPE exceeds that of LDPE. PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV irradiation. The kinetics associated with the formation and termination of peroxy  $RO_2^*$  and fluorocarbon long-lifetime radicals was studied. It is mainly middle peroxy radicals that are formed at treatment conditions close to those used in industrial processes.

### La cinétique et le mécanisme de la fluorisation directe des polyéthylènes

Deux types de polyéthylène de basse densité (LDPE), cinq types de polyéthylène de haute densité (HDPE), le poly(vinyle fluorure) (PVF) et le poly(vinylidène fluorure) (PVDF) ont été étudiés. La fluorisation du LDPE et du HDPE est un procédé à diffusion contrôlée et se déroule au moyen d'un mécanisme à chaîne branchée qui se produit après une période d'induction. L'initiation de l'action se produit au moyen de la réaction du fluor moléculaire avec la liaison C-H. Le taux de la fluorisation des HDPE excède celui des LDPE. Le PVDF ne peut pas être fluoré même à des températures aussi élevées que 430K et/ou sous irradiation UV. On a étudié la cinétique associée à la formation et à la terminaison du peroxy  $RO_2^*$  et des radicaux fluorocarbène à longue durée de vie. Ce sont pour la plupart des radicaux peroxy centraux qui sont formés sous des conditions de traitement qui sont proches de celles des procédés industriels.

### Die Kinetik und Mechanismus der direkten Fluorinierung von Polyethylenen

Zwei Arten von Polyethylen mit niedriger Dichte (LDPE), fünf Arten mit hoher Dichte (HDPE), sowie Polyvinyl-Fluorid (PVF) und Polyvinylidene-Fluorid (PVDF) wurden untersucht. Die Fluorinierung von LDPE und HDPE ist ein diffusionskontrollierter Prozeß, der durch eine verzweigte Kettenreaktion nach einer Induktionsperiode abläuft. Der Prozeß wird durch die Reaktion von molekularem Fluorin mit der C-H Verbindung in Gang gesetzt. Die Fluorinierungsrate von HDPE ist größer, als die von LDPE. PVDF kann selbst bei hohen Temperaturen (430 °K) und/oder UV-Licht nicht fluoriniert werden. Wir erforschten auch die Kinetik der Formation und Terminierung von Peroxy  $RO_2^*$  und die langlebigen Fluorkarbonradikale. Unter den in Industrieprozessen üblichen Operationsbedingungen werden vor Allem die mittleren Peroxyradikale gebildet.

## For correspondence contact

A P Kharitonov

Institute of Energy Problems of Chemical Physics (Branch) of the Russian Academy of Sciences, Chernogolovka, Moscow Region, 142432, Russia

Email: khariton@binep.ac.ru

Copyright OCCA 2005

## Introduction

Surface modification is a well-established method for enhancing the performance of polymeric materials in a number of applications,<sup>1</sup> and one of the more effective methods of surface modification is direct fluorination (ie the treatment of a polymer surface with gaseous fluorine or a fluorine-containing mixture). Due to relatively weak F-F bonds and strong C-F bonds, fluorination can proceed at a rate acceptable for industrial processes at ambient temperatures without the need for any initiation process.<sup>1-3</sup> An important practical application of direct fluorination is the enhancement of the barrier properties of industrial polymer components. As an example, the fluorination of plastic gasoline automobile tanks can result in an approximately one hundred-fold decrease in the loss of fuel from a tank when compared with that from virgin, untreated tanks.<sup>1,4</sup> Such an enhancement enables compliance with legislation relevant to the permeation of volatile organic compounds from automobile fuel tanks into the general environment. It is worth noting that under industrial conditions, a surface layer of only around 0.1 to 10  $\mu\text{m}$  in thickness is modified during the fluorination process and the bulk of the polymer remains unchanged.

The majority of research in this field has until recently been mainly concerned with the practical applications of direct fluorination and only a limited number of investigators have focused upon the fundamental aspects of the direct fluorination of polyethylene. In addition, there seems to be a number of discrepancies between the various findings as reported in the literature.

According to some authors, the fluorination of polyethylene (PE) results in the total replacement of hydrogen atoms with fluorine to form a PTFE (polytetrafluoroethylene)-like structure  $(-\text{CF}_2-\text{CF}_2-)_n$ .<sup>5,6</sup> However, such a modification requires a considerable amount of time (ie from several weeks to several months). An almost complete degree of substitution of H- with F-atoms was reported by Hara, Fukumoto and Watanabe<sup>7</sup> for HDPE films (UltZex2021L from Mitsui ekiyu Kagaku Kogyo) which had been subjected to a treatment time of 15 hours at 0.2 bar  $\text{F}_2$  pressure with a temperature of 100°C; conditions which are distant from those in an industrial environment. Other authors have found that the fluorination of PE within a commercially acceptable timescale (ie of around one hour) did

not result in the total replacement of the H-atoms (ie the maximum possible ratio of F/C = 2 was never attained). Examples of this include work by Corbin *et al* who found that surface fluorination led to a surface F/C ratio of only 0.84 following treatment with a 5% $\text{F}_2$ /95%Ar mixture for one hour at room temperature.<sup>8</sup> Similarly, a range of F/C ratios have been reported, following treatment with a variety of mixtures, including 1.69,<sup>5</sup> 1.33,<sup>9</sup> and 1.5.<sup>10</sup> Similarly, the fluorination of PVF as reported by Corbin *et al*<sup>8</sup> did not result in the total substitution of H-atoms for F-atoms but only led to the formation of a polymer on the surface with a F/C ratio of 0.70 after treatment with a 5%  $\text{F}_2$ /95% Ar mixture at STP (standard temperature and pressure) for one hour.<sup>8</sup> Shinohara *et al*<sup>11</sup> noted a F/C ratio of only 1.25 after treatment with 300 to 800 Torr of fluorine at room temperature, although the  $\text{F}_2$  used in these studies contained around 1.6% of oxygen.

No change of surface chemical composition was found following fluorination of PVDF<sup>8</sup> and no mass change was detected upon fluorination of PVDF *in situ*.<sup>12</sup> However, on the contrary, according to Scherer *et al*,<sup>13</sup> the chemical composition of PVDF may be changed through fluorination to give a F/C ratio of 1.9.

The presence of oxygen in a fluorinating mixture, either through controlled addition or as an intrinsic contaminant, results in the formation of carboxylic acid  $-\text{C}(\text{O})\text{F}$  groups which are themselves transformed into carbonyl  $-\text{C}(\text{O})\text{OH}$  groups upon contact with water vapour. The concentration of  $-\text{C}(\text{O})\text{F}$  groups in LDPE<sup>2</sup> can reach  $1.8 \cdot 10^{-2} \text{ mole} \cdot \text{g}^{-1}$ .

The kinetics of formation of fluorinated layers has been studied by a number of investigators, although no measurements were carried out *in situ* (ie during the fluorination process). All measurements were carried out in such a manner that fluorination was halted, and the sample then removed from the reaction vessel following which the measurements were carried out. Attenuated total reflectance spectroscopy has been used to measure the thickness  $\delta_f$  of fluorinated layers of HDPE.<sup>14</sup> The authors proposed a linear dependence between  $\delta_f$  and the time of fluorination  $t$  but when the results were converted by the authors of this paper into a  $\log(\delta_f)-\log(t)$  scale, the following relationship was obtained:  $\delta_f \sim t^{0.70}$ . The fluorinated layer of a sample of PE was separated from untreated polymer by boiling in xylene<sup>10</sup> and the experimentally determined dependence between

$\delta_f$  and  $t$  was close to  $\delta_f \sim (\rho_f \cdot t)^{0.5}$ , where  $\rho_f$  is the fluorine partial pressure. A quartz crystal microbalance technique was used to measure the dependence of the mass of HDPE films on the treatment time *in situ*.<sup>7</sup> A mixture of 5 to 20% of  $\text{F}_2$  in Ar was used to carry out fluorination over a temperature range between 27 and 100°C. During the initial stages (ie the first few minutes), the rate of fluorination was very slow, but subsequently the increase in the mass of the film became proportional to the square root of the fluorination time when the fluorine partial pressure and temperature were held constant. Unfortunately, the calculations of the activation energy associated with the rate of fluorination were not correct as the authors took into account only fluorine diffusion and not fluorine consumption during the course of the chemical reactions. The change of polymer film weight during fluorination was monitored *in situ*.<sup>12</sup> LDPE (density 0.921g  $\text{cm}^{-3}$  from Plastomark), HDPE (density 0.950g  $\text{cm}^{-3}$  from AECL), PVF, PVDF, polypropylene (PP, density 0.907g  $\text{cm}^{-3}$  from Sasol Polymers), and a copolymer of PE and PP (PP-co-PE, density 0.900g  $\text{cm}^{-3}$  from Sasol Polymers) were used. Mixtures containing 5 and 10% of  $\text{F}_2$  and He,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  at ambient pressures were used for treatment over a range between 28 and 70°C. Again it was found<sup>7</sup> that during the initial stages (ie within one to two minutes) the rate of fluorination was very slow, but subsequently the increase in mass became proportional to the square root of the time of fluorination. The increase of the concentration of fluorine in a fluorination mixture and elevation of treatment temperature resulted in a significant increase in the rate of fluorination. The replacement of  $\text{N}_2$  with He resulted in a slight decrease of the fluorination rate but  $\text{O}_2$  strongly inhibited the reaction. No reaction was detected between  $\text{F}_2$  and PVDF at 50°C for one hour. The rate of fluorination was noted to increase in the order LDPE < PVF < HDPE < (PP-co-PE) < PP. Nazarov *et al*<sup>15</sup> studied the dependence of the mass increase for HDPE, LDPE and PP on the time of fluorination and showed that the rate of fluorination increased with fluorine concentration and in the order HDPE < LDPE < PP. Oxygen was found to strongly inhibit the reaction with an increase in oxygen concentration in the fluorinating mixture from 0.1 to 1 volume percentage resulting in an almost ten-fold decrease in the fluorination rate.

It was noted that long-lifetime peroxy  $\text{RO}_2$ , and possibly perfluoroalkyl radicals, are formed as end-point products

of the direct fluorination of PE.<sup>16–18</sup> The concentration of peroxy radicals was estimated,<sup>16</sup> in the case of PE, as between (2...3)  $10^{18}$  and (2...5)  $10^{17}$  radicals. $\text{g}^{-1}$ .<sup>18</sup> However, it should be emphasised that the experiments were carried out with thick PE samples which were not fluorinated to their full thickness. The radical concentration was then estimated over the complete sample, not distinguishing between its fluorinated surface layer and its non-fluorinated part. The lifetime of the radicals in fluorinated polymers was not reported.

On the basis of the above literature review, the following summary can be made. There seems to be no direct experimental confirmation of the existence of a sharp thin boundary transition zone between fluorinated and untreated PE layers and no evidence that the direct fluorination of PE occurs as a diffusion-controlled reaction. In addition, the relationship between the thickness of a fluorinated layer and the time of fluorination has not been determined *in situ*. Only the gross chemical compositions (ie the ratios of F/C/O/N) have been studied and minor chemical compositional changes ignored. Neither the actual concentration of long-life radicals inside a fluorinated layer nor their termination kinetics have been measured. Transient species, such as radicals of a relatively short lifetime which take part in the chain continuation processes, have not been monitored or identified, and a scheme to describe the elementary stages of a fluorination process has only been proposed and not verified through experimentation.

This paper will provide further insight into the details of the reaction of polyethylene and fluorine, with reference to the research described in earlier publications.<sup>19–21</sup>

## Materials

The fluorine used in the work reported here contained less than 0.1 volume percent of oxygen. For a particular set of experiments, the additional purification of fluorine was carried out using the method of Shamir and Binenboym.<sup>22</sup> A mixture of  $\text{F}_2$  and  $\text{SbF}_5$  was irradiated inside a stainless steel vessel by ultraviolet (UV) light from a mercury lamp for one hour through a sapphire optical window. Residual  $\text{O}_2$  was removed by the reaction of  $\text{F}_2$ ,  $\text{O}_2$  and  $\text{SbF}_5$  to form solid  $\text{O}_2\text{SbF}_6$ . Nitrogen and helium used in this work were of 99.995% purity. Two types of LDPE (densities 0.926g  $\text{cm}^{-3}$  and 0.918g  $\text{cm}^{-3}$  from Aldrich), five types of HDPE marked by figures no 1 – BP (density 0.947g  $\text{cm}^{-3}$ , melt index

(190C/21.6): 6.1g/10 minutes, colourless), no 2 – Elenac (density 0.945g  $\text{cm}^{-3}$ , melt index (190C/21.6): 6g/10 minutes, colourless), no 3 – Atofina (density 0.949g  $\text{cm}^{-3}$ , high load melt index: 8.0g/10 minutes, black), no 4 – Borealis (density 0.948g  $\text{cm}^{-3}$ , melt index (190C/21.6): 7.0g/10 minutes, colourless/UV stabilised), no 5 – Solvay (density 0.946g  $\text{cm}^{-3}$ , high load melt index: 4.2g/10 minutes, contains 0.2% of carbon black), PVF (poly(vinyl fluoride) (Scientific Polymer Products Inc, Ontario, Canada), and PVDF (poly(vinylidene fluoride) (Fluorochem Limited, Derbyshire, UK) were used. A set of flat films with a very smooth and reflective surface was prepared with a hot press. In some experiments, LDPE was used in the form of a cotton wool. This was fabricated by dropping a solution of LDPE in hot oxylene into ethanol. The precipitate was then allowed to dry at an elevated temperature.

## Experimental

An original kinetic interference method using visible light was used to investigate the relationship between the resulting thickness of a fluorinated layer  $\delta_F$  and the duration of the fluorination process.<sup>23–30</sup> Very flat films of high reflectance were used and the intensity  $I$  of a light (at a fixed wavelength  $\lambda=0.6328\mu\text{m}$ ) reflected at a  $45^\circ$  angle from the surface of the polymer film (which had been treated in the reaction vessel by fluorine) was monitored. If the untreated and fluorinated polymer layers are separated by a very thin transition (boundary) layer parallel to the upper polymer surface (see Figure 2: thickness of this boundary layer must be much smaller than  $\lambda/4$ ) (ie the fluorinated layer thickness was uniform across the polymer surface), the intensity  $I$  of light (at a fixed wavelength  $\lambda$ ) has interference features (ie the intensity of light depends on time and consists of a series of maxima and minima – see Figure 3 in reference 28). These interference features are due to the interference of two light beams: (a) reflected from the fluorinated film surface- gaseous phase boundary; and (b) reflected from the fluorinated film-untreated film boundary. The first minimum corresponds to the thickness of the anti-reflecting layer (fluorinated layer thickness  $\delta_F = b \cdot (1/4) \cdot \lambda / n_F$  where  $n_F$  is the refractive index of the fluorinated polymer, coefficient  $b = [1 - (\sin\beta)^2(n_F)^{-2}]^{0.5}$  takes into account the refraction of the beam falling at the angle  $\beta$  on the surface of a polymer films (in the authors' experiments  $\beta = 45^\circ$ ), the first maximum corresponds to  $\delta_F = b \cdot (1/2) \cdot \lambda / n_F$  and so on.<sup>27</sup>

This method allows the measurement of the thickness of the fluorinated layer from  $\delta_F \sim 0.13\mu\text{m}$  for  $\lambda = 0.6328\mu\text{m}$  (a He-Ne laser was used as a light source; the upper limit of the  $\delta_F$  value depends on the type of polymer under study; for example, in the case of polystyrene it exceeded  $50\mu\text{m}$ ).<sup>28</sup> The main advantage of this method is that it is non-destructive and the relationship between the thickness  $\delta_F$  of the fluorinated layer with time can be monitored *in situ* (ie the fluorination procedure is not interrupted by the measurement process). A Speko-rd UV-VIS (Karl Zeiss Jena) spectrometer was used to measure spectra in the visible region. Visible spectra have equidistant (in wavenumber scale) interference features and these spectra were used to calculate the thickness of the fluorinated layer of the fluorinated films. To measure spectra in the infrared (IR) region, a FTIR spectrometer FT-02 (Lumex, Russia) was used. At least 100 scans (usually at  $4\text{cm}^{-1}$  resolution) were collected to obtain a single IR spectrum. A special reaction vessel equipped with ZnSe optical windows (stable to fluorine action and transparent over  $\sim 20,000$  to  $500\text{cm}^{-1}$ ) was developed and fabricated. This reaction vessel allowed measurement of the spectra of fluorinated films in a vacuum (ie to minimise the influence of atmospheric moisture). An electron spin resonance (ESR) spectrometer SE/X 2544 (Radiopan) was used to monitor ESR spectra and this was connected directly to a sampling system to allow for the direct introduction of fluorine into the reaction vessel located within the ESR resonator, and again enable the study of the kinetics of fluorination *in situ*. ESR spectra could be measured over a 77 to 295K temperature interval. VLR-200 balances were used to measure weight with an accuracy of 0.5mg, and a repeatability of 0.05mg.

## Results and Discussion

### Kinetics of formation of a fluorinated layer

The visible spectra (0.4 to  $0.7\mu\text{m}$ ) of fluorine-treated PE films (HDPE and LDPE) have a distinct interference structure (see Figure 1). These spectra can be explained using a multilayer model of a fluorinated polymer film, as previously reported.<sup>28,30</sup> If the film is treated simultaneously on both sides, the fluorinated film consists of (1) a fluorinated layer, (2) a boundary transition layer, and (3) a virgin, untreated layer (see Figure 2). Interference features can arise only in the case when the thickness  $\delta_b$  of a boundary transition layer is much less than

$\lambda/(4 \cdot n_F)$ , where  $\lambda$  is the wavelength of visible light and  $n_F$  (for the majority of fluorinated polymers  $n_F \sim 1.35$  to 1.45) is the refraction index of the fluorinated layer in the visible region of the spectrum. Hence, it can be estimated that  $\delta_b \leq 0.07\text{mm}$  and that direct fluorination can be considered a surface phenomenon (ie the reaction proceeds as a diffusion-limiting process). The majority of the chemical reactions occur inside this transition boundary layer and the majority of the physical and chemical properties such as density, refraction index, chemical composition etc of the polymer are mainly only changed within this layer. The rate of formation of the fluorinated layer is limited by the permeation rate of fluorine from the gaseous phase penetrating through the fluorinated layer into the virgin layer. In this case the kinetic interference method previously described can be applied.

The dependence of the thickness  $\delta_F$  of a fluorinated layer on the time of fluorination  $t$  in the case of LDPE (density  $0.926\text{g cm}^{-3}$ ) is shown in Figure 3. The data points ( $\delta_F = 0, t = 0$ ) are ignored in order to facilitate linear regression. Similar dependences were obtained in the treatment of LDPE (density  $0.926\text{g cm}^{-3}$ ) with 9.7%  $F_2 + 90.3\%$  He mixture and in the treatment of LDPE (density  $0.918\text{g cm}^{-3}$ ) with undiluted fluorine. When a fluorinated layer of a thickness of  $\sim 0.1\mu\text{m}$  is formed, the  $dF$  value depends on the square root of the time of fluorination  $t$ :

$$\delta_F = A \cdot t^{0.5} + b \quad \text{Equation 1}$$

The following quantitative expressions can be obtained from the experimental data ( $p_F$  - in bars,  $t$  - in seconds):

LDPE, density  $0.926\text{g cm}^{-3}$ , treatment with undiluted fluorine:

$$\delta_F = 4.27 \cdot 10^{-4} \cdot p_F^{0.56} \cdot t^{0.5}$$

LDPE, density  $0.926\text{g cm}^{-3}$ , treatment with 9.7%  $F_2 + 90.3\%$  He mixture:

$$\delta_F = 4.07 \cdot 10^{-4} \cdot p_F^{0.57} \cdot t^{0.5}$$

LDPE, density  $0.918\text{g cm}^{-3}$ , treatment with undiluted fluorine:

$$\delta_F = 6.46 \cdot 10^{-4} \cdot p_F^{0.52} \cdot t^{0.5}$$

The dependence of factor A on the fluorine partial pressure  $p_F$  for the two types of LDPE and for various fluorinating mixtures (undiluted fluorine and 9.7%  $F_2 + 90.3\%$  He) are shown in Figure 4. The experimental results lead to the conclusion that even a tenfold dilution of fluorine with an inert gas does not significantly influence the rate of formation of a fluorinated layer on either heavier LDPE types ( $0.926\text{g cm}^{-3}$ ) or on the less

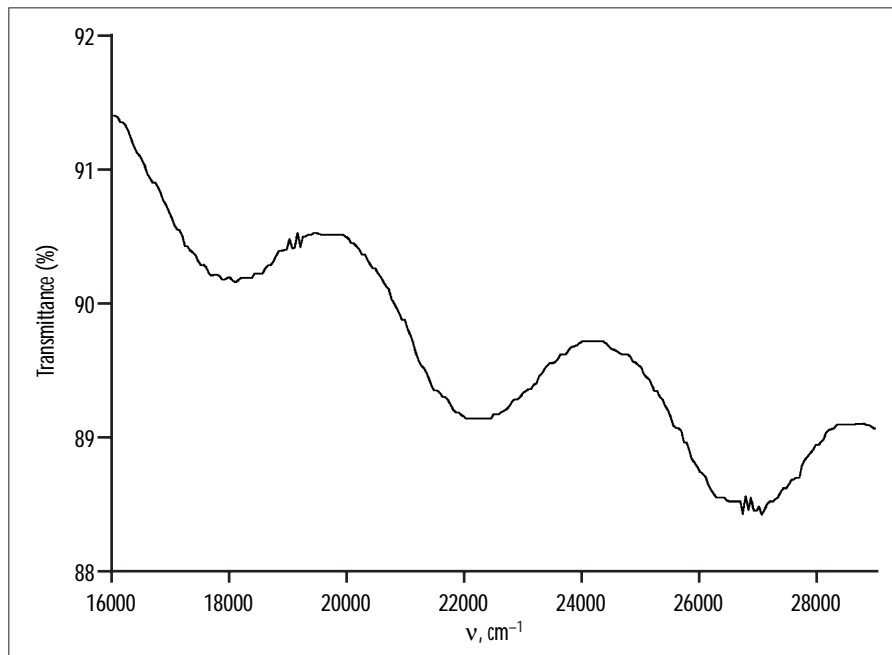


Figure 1: Transmittance of fluorinated LDPE flat film versus wavenumber  $\nu$

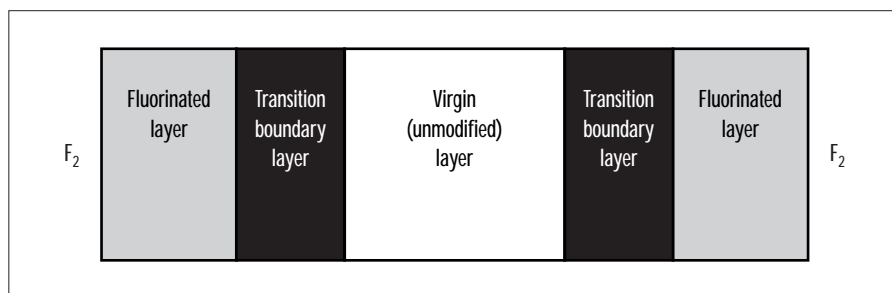


Figure 2: Cross-cut of a polymer film treated with fluorine

dense LDPE types ( $0.918\text{g cm}^{-3}$ ). The experiments prove, however, that the rate of fluorination is proportional to the density of the chosen LDPE under examination. In this context it should be noted that none of the linear regressions obtained from the results of actual experiments crossed the origin of the coordinate system ( $\delta_F = 0, t = 0$ ) but intersected the  $t$ -axis at  $t = (1-3)$  minutes. Similar results have been reported elsewhere.<sup>7,12</sup>

The dependence of the thickness  $\delta_F$  of a fluorinated layer on the fluorination time  $t$  for the HDPE sample nos 1 to 5 is shown in Figure 5 along with the results obtained with the LDPE ( $0.926\text{g cm}^{-3}$ ), LDPE ( $0.918\text{g cm}^{-3}$ ) and PVF. In either case, the data points ( $\delta_F = 0, t = 0$ ) were ignored in order to facilitate linear regression.

In contrast, all the attempts to effect the fluorination of PVDF were unsuccessful. PVDF was treated (a) with a 20%  $F_2/80\%$  He mixture (total mixture pressure 1 bar) at  $T = 293\text{K}$  for four hours; (b) with a 20%  $F_2/80\%$  He mixture (total mixture pressure 1 bar) at  $\sim 420\text{K}$  for four hours;

and (c) with a 20%  $F_2/80\%$  He mixture (total mixture pressure 1 bar) at 293K for ten hours under UV irradiation from a mercury discharge lamp (electric power 250W). The experiments did not result in any change in the IR spectra of the relevant polymer samples nor in any change in the sample weights. The experiments prove that PVDF resists fluorination even under rather extreme reaction conditions.

The influence of the treatment temperature on the rate of formation of fluorinated surface layers on polyethylene was studied in experiments with fluorine-nitrogen blends with 10% fluorine concentration (see Figures 6 and 7). While the total gas pressure in all experiments was 1 bar, a, treatment temperatures between 297.7 and 341.2K (24.5 to 68°C) were applied. The treatment time  $t$  was between  $\sim 3$  and 5 hours. As mentioned above, diluting the fluorine with inert gas had virtually no effect upon the rate of the fluorination reaction. Also, nitrogen only slightly affected the reaction rate of surface fluorination. In addition, a typical induction period was observed which lasted until the flu-

orinated surface layer had reached a thickness of  $\delta_F \sim 0.13 \mu\text{m}$ . Beyond that, surface layer formation proceeded with the square root of the treatment time, according to Equation 1.

The dependence of the pre-exponential coefficient  $A$  ( $\mu\text{m}\cdot\text{s}^{-0.5}$ , see Equation 1) on the treatment temperature  $T$  (K) is shown in Figure 5 and can be described as follows:

$$A = 0.59 \cdot 10^{-(597/T)} \quad \text{Equation 2}$$

### Kinetics of formation of fluorinated layer – Summary

- The fluorination of polyethylene proceeds via a branched chain mechanism following an induction period.
- The fluorination of LDPE and HDPE is a diffusion-controlled process. This indicates that the rate of formation of a fluorinated layer is limited by the rate of penetration of fluorine through the fluorinated polymer layer into the untreated layer. The fluorinated and untreated layers are separated by a very thin transient boundary layer where the majority of the chemical reaction takes place.
- The rate of formation of a fluorinated layer increases with fluorine partial pressure and temperature and was not observed to be affected by the presence of He and/or  $\text{N}_2$  in the fluorinating mixture.
- There is practically no correlation in the rate of formation of the fluorinated layer with the actual density of the HDPE or with the presence of additives such as carbon black.
- The rate of fluorination of HDPE significantly exceeds that of LDPE.
- PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV irradiation.
- The fluorination rate of PVF is almost identical to the fluorination rate of LDPE.

### The relationship between fluorination and chemical composition: IR study

Two types of LDPE with a density of 0.926 and 0.918  $\text{g cm}^{-3}$  were studied by IR spectroscopy. Band assignments were made on the basis of Socrates.<sup>31</sup>

#### LDPE with density 0.926 $\text{g cm}^{-3}$

Figure 8 shows (1) the spectra of virgin LDPE; (2) the spectra of surface-fluorinated LDPE ( $\delta_F = 0.39 \mu\text{m}$ ) treated at room temperature with undiluted fluorine at a fluorine partial pressure of  $p_F =$

147 Torr, for  $t = 85$  minutes; and (3) the spectra of surface-fluorinated LDPE ( $\delta_F = 0.75 \mu\text{m}$ ) treated for  $t = 16$  hours, at room temperature and 1 bar total gas pressure with a three-component mixture consisting of 2.8% fluorine, 9.4% oxygen and 87.8% helium, at a total pressure of 1 bar ( $p_F = 70$  Torr). It is pertinent to note that the spectra shown in Figure 8 were measured repeatedly for several hours following fluorination (ie during this period all the samples were in contact with atmospheric air for several hours and were thus subjected to hydrolysis).

The action of fluorine substantially changes the IR spectra of the virgin LDPE

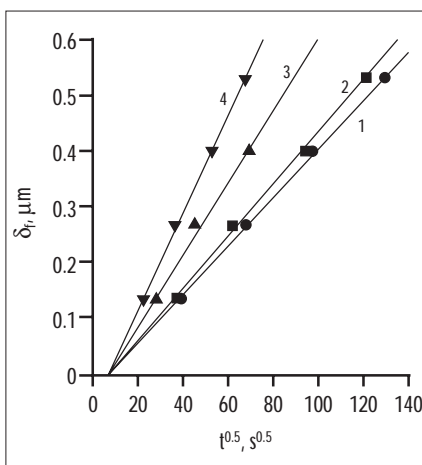


Figure 3: Dependence of the thickness  $\delta_F$  ( $\mu\text{m}$ ) of a fluorinated layer on fluorination time  $t$  (s) in the case of LDPE with a density of 0.926  $\text{g cm}^{-3}$ . All treatments were with undiluted fluorine and curves 1 to 4 correspond to the fluorine pressures of 58.8, 88.2, 147 and 205.8 Torr, respectively. Treatment temperature: 293.5  $\pm$  0.5K. Data points at ( $\delta_F = 0$ ,  $t = 0$ ) were ignored to facilitate linear regression

films. Moreover, it was clear from the changes in the IR spectra that reactive components present in the fluorinating mixture influenced the chemical composition of a fluorinated surface layer. The main feature in the IR spectra of LDPE treated with undiluted fluorine is a very broad diffuse band over the 1000 to 1300  $\text{cm}^{-1}$  region. Two maxima within that band located at 1183 and 1148  $\text{cm}^{-1}$  are due to the absorption of C–F, FCF and  $\text{F}_2\text{CF}$  bonds. This means that a substantial quantity of partially fluorinated groups (eg  $-\text{CHF}-$ ) are present in a fluorinated polymer. The intensity of the diffuse band increases with the thickness of the fluorinated layer. The spectrum of LDPE treated with an oxygen-containing  $\text{F}_2/\text{He}$  mixture substantially differs from

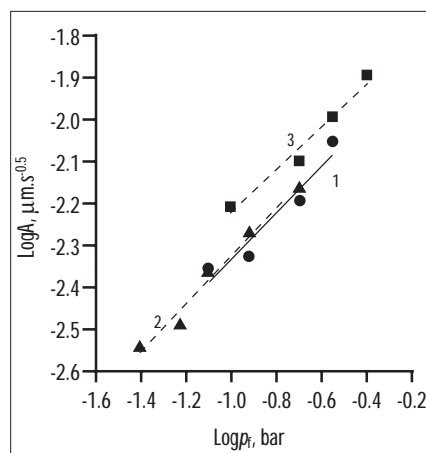


Figure 4: The dependence of the value of  $A$  ( $\mu\text{m}\cdot\text{s}^{-0.5}$ ) (see Equation 1) on fluorine partial pressure  $p_F$  (Torr). 1: – LDPE density 0.926  $\text{g cm}^{-3}$ , treatment with undiluted fluorine; 2: triangles – LDPE density 0.926  $\text{g cm}^{-3}$ , treatment with mixture 9.7%  $\text{F}_2/90.3\%$  He; 3: squares – LDPE density 0.918  $\text{g cm}^{-3}$ , treatment with undiluted fluorine

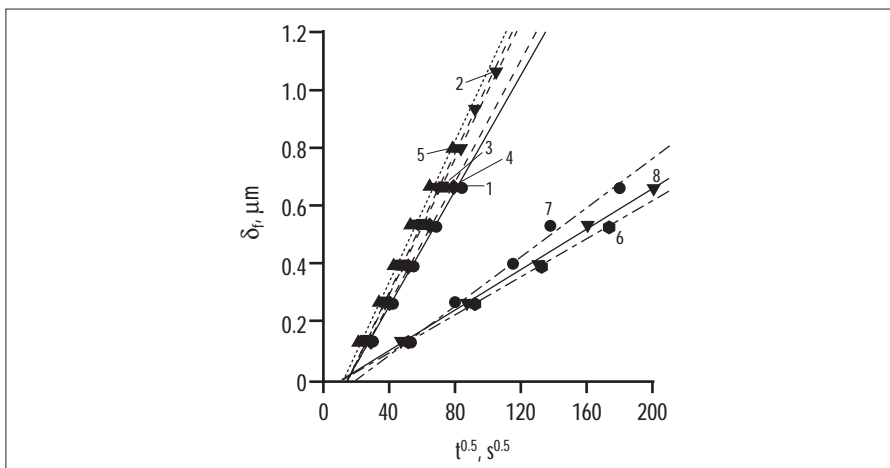


Figure 5: The dependence of the thickness  $\delta_F$  ( $\mu\text{m}$ ) of a fluorinated layer on the time of fluorination  $t$  (s). Treatment with undiluted fluorine at  $p_F = 35.3$  Torr. 1 to 5: HDPE marked by numbers 1 to 5 correspondingly; 6: LDPE density 0.926  $\text{g cm}^{-3}$ ; 7: LDPE density 0.918  $\text{g cm}^{-3}$ ; 8: PVF. Treatment temperature: 293  $\pm$  1K. Data points at ( $\delta_F = 0$ ,  $t = 0$ ) were ignored to facilitate linear regression

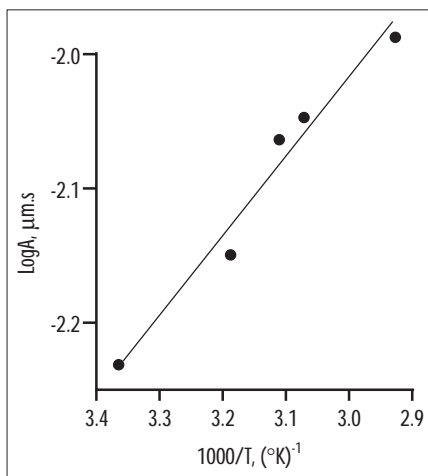


Figure 7: Dependence of the pre-exponential factor  $A$  ( $\mu\text{m}\cdot\text{s}^{-0.5}$ ) (see Equation 1) on the reciprocal of treatment temperature  $T$  (semi logarithmic scale) for the data shown in Figure 6

the spectrum of LDPE treated with undiluted, pure fluorine. At first the absorption maximum of the previously mentioned diffuse band system shifts to  $1093\text{cm}^{-1}$ . The shift can be associated with the preferred formation of mono-fluorinated compounds such as  $-\text{CHF}-$  and  $-\text{C}(\text{O})\text{F}-$ . The formation of  $\text{C}=\text{O}$  bonds is evident from the appearance of the bands between  $1600$  to  $1900\text{cm}^{-1}$ . A more detailed discussion on those bands will be presented.

An unsupported film of LDPE (density  $0.926\text{g cm}^{-3}$ ) was treated with an oxygen-containing fluorine blend in the ratio  $\text{O}_2/\text{F}_2/\text{He} = 1\%/10\%/89\%$  at a total pressure of 1 bar and  $T = 293\text{K}$ . The IR spectra of the untreated, virgin and treated samples are shown in Figure 9. The band over the range  $2290$  to  $2375\text{cm}^{-1}$  can be ignored due to the IR

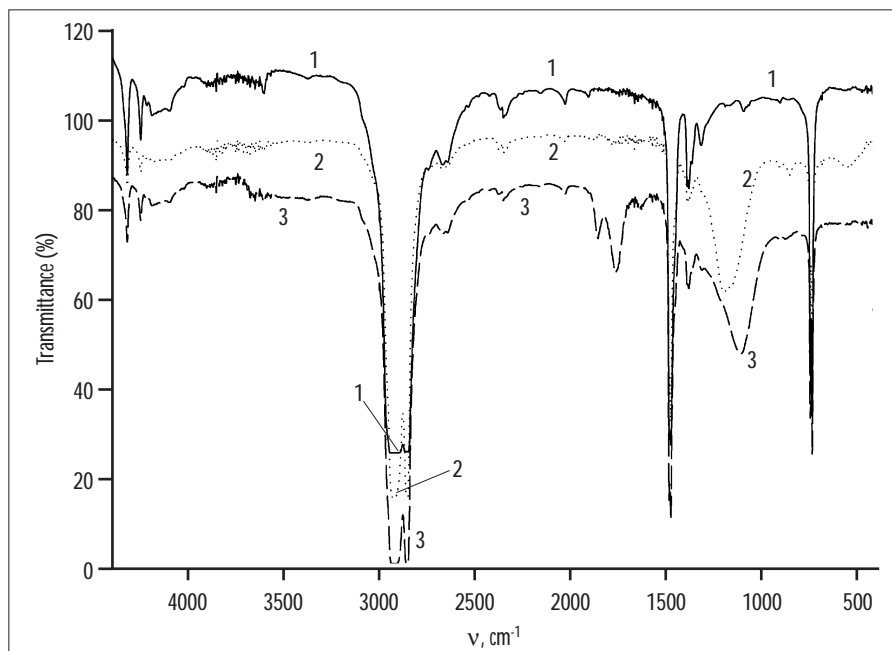


Figure 8: IR spectra of virgin and treated LDPE (density  $0.926\text{g cm}^{-3}$ ). 1: virgin LDPE; 2: LDPE treated with undiluted  $\text{F}_2$  ( $p_{\text{F}} = 147$  Torr, treatment time  $t = 85$  minutes at  $T = 293\text{K}$ , thickness of fluorinated layer  $\delta_{\text{F}} = 0.39\mu\text{m}$ ); 3: LDPE treated with a  $\text{O}_2/\text{F}_2/\text{He} = 2.8/9.4/87.8\%$  mixture. Total pressure 1 bar,  $p_{\text{F}} = 70.2$  Torr,  $t = 16$  hours at  $T = 293\text{K}$ ,  $\delta_{\text{F}} = 0.75\text{mm}$ . Curves were shifted along the Y axis to prevent overlapping

absorption by  $\text{CO}_2$  in the gas phase. Diffuse bands over  $\sim 1000$  to  $1400\text{cm}^{-1}$  corresponded to various C-F absorptions. To separate overlapping bands, computer simulation was applied. It was clearly evident that in freshly fluorinated samples (ie treated with mixtures of  $\text{F}_2/\text{O}_2$ ), four bands at  $1853$ ,  $1762$ ,  $1741$  and  $1622\text{cm}^{-1}$  arose.

The absorption at  $1853\text{cm}^{-1}$  can be attributed to a carbonyl vibration in a  $-\text{C}(\text{O})\text{F}$  group. The band at  $1762\text{cm}^{-1}$  can be assigned to the  $\text{C}=\text{O}$  vibration in the  $\alpha$ -fluoro-ketone  $-\text{CHF}-\text{C}(\text{O})-\text{CHF}-$  while the band at  $1741\text{cm}^{-1}$  can be attributed

to the  $\text{C}=\text{O}$  vibration in the  $\alpha$ -fluoroester  $-\text{CHF}-\text{C}(\text{O})-\text{O}-$  or the  $\alpha$ -fluoro-ketone  $-\text{CH}_2-\text{C}(\text{O})-\text{CHF}-$ .

A weak band at  $1622\text{cm}^{-1}$  can be attributed to both  $\text{C}=\text{O}$  vibration in the enol form of the  $\beta$ -diketones  $-\text{C}(\text{O})-\text{CF}=\text{C}(\text{OH})-$  or the double bond  $\text{C}=\text{C}$  (eg  $-\text{FC}=\text{CH}-$ ) stretching vibration.

After hydrolysis (see curve 3), three new absorptions at  $1736$ ,  $1653$  and  $1623\text{cm}^{-1}$  arose; to separate the bands, the above-mentioned computer simulation was applied, while the band at  $1853\text{cm}^{-1}$  disappeared as result of the acid fluoride hydrolysis:  $-\text{COF} + \text{H}_2\text{O} \Rightarrow \text{COOH} + \text{HF}$ .

The  $1736\text{cm}^{-1}$  band was probably the  $\text{C}=\text{O}$  vibration in either  $-\text{CHF}-\text{C}(\text{O})\text{OH}-$  or the  $\alpha$ -fluoroester  $-\text{CHF}-\text{C}(\text{O})-\text{O}-$  or the  $\alpha$ -fluoroaldehyde  $-\text{CHF}-\text{C}(\text{O})\text{H}$  or the  $\alpha$ -fluoro-ketone  $-\text{CH}_2-\text{C}(\text{O})-\text{CHF}-$ .

Newly formed  $\text{C}=\text{C}$  bonds were most likely responsible for the absorption at  $1653\text{cm}^{-1}$ . The band at  $1623\text{cm}^{-1}$  can be assigned to both the  $\text{C}=\text{O}$  vibration of the enol form of the  $\beta$ -diketones  $-\text{C}(\text{O})-\text{CF}=\text{C}(\text{OH})-$  and to the double bond  $\text{C}=\text{C}$  (eg  $-\text{FC}=\text{CH}-$ ) stretching vibration.

#### LDPE with density $0.918\text{g cm}^{-3}$

The IR spectra and chemical composition of fluorinated LDPE with a density of  $0.918\text{g cm}^{-3}$  were very similar to that

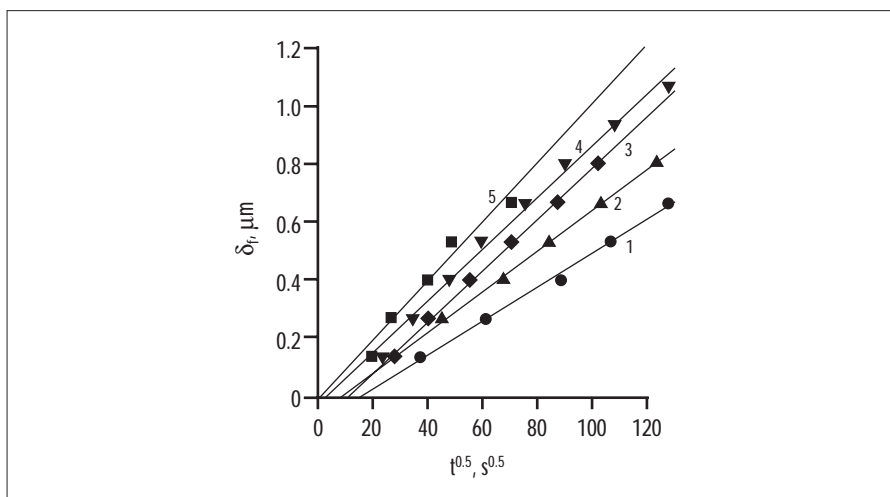


Figure 6: Dependence of the thickness  $\delta_{\text{F}}$  ( $\mu\text{m}$ ) of a fluorinated layer on fluorination time  $t$  (s). LDPE density  $0.918\text{g cm}^{-3}$ . Fluorinating mixture:  $10\% \text{F}_2/90\% \text{N}_2$ . Total mixture pressure was equal to 1 bar. Treatment temperature  $T$  was equal to  $297.7$ ,  $313.2$ ,  $321.7$ ,  $325.7$  and  $341.2\text{K}$  ( $24.5$ ,  $40.5$ ,  $48.5$ ,  $52.5$  and  $68^\circ\text{C}$ ) for curves 1 to 5 respectively. Data points at  $\delta_{\text{F}} = 0$ ,  $t = 0$  were ignored to facilitate linear regression

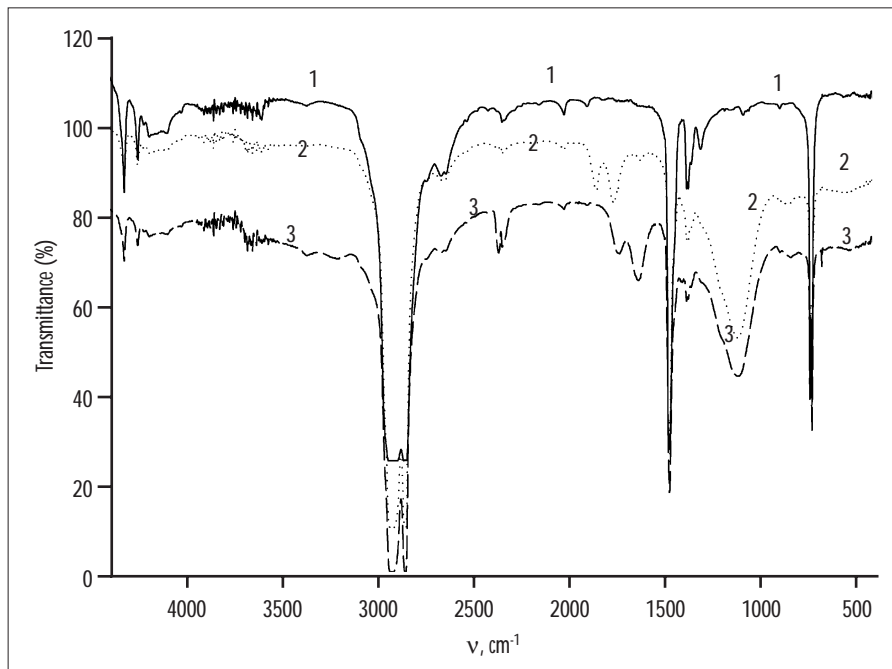


Figure 9: IR spectra of virgin and treated LDPE (density  $0.926 \text{ g cm}^{-3}$ ). 1: virgin LDPE; 2: LDPE treated with an  $\text{O}_2:\text{F}_2:\text{He}$  mixture of a ratio of 1:9.7:89.3 (total pressure 1 bar,  $p\text{F} = 70.2 \text{ Torr}$ ,  $t = 16 \text{ hours}$  at  $T = 293\text{K}$ ,  $\delta_{\text{F}} = 0.81 \mu\text{m}$ ), spectrum measured three minutes after removal of the film from the reactor; 3: the same film following two months of storage in ambient air. The curves were shifted along the Y axis to minimise overlapping

**Table 1: Concentration  $N_{\text{C=O}}$  of carbonyl groups in LDPE treated under different conditions. Films were treated on both sides so that a double thickness of fluorinated layer was used in the calculations. The fluorine contained  $\sim 0.1$  volume percent of oxygen as contaminant**

LDPE density ( $\text{g cm}^{-3}$ )	Fluorination mixture	Mixture pressure (bar)	$N_{\text{C=O}}$
0.926	$\text{O}_2:\text{F}_2:\text{He} = 1:10:89$	1	0.49
0.926	$\text{O}_2:\text{F}_2:\text{He} = 2.8:10:87.2$	1	0.48
0.918	$\text{O}_2:\text{F}_2:\text{He} = 0.4:10:89.6$	1	0.27
0.918	$\text{O}_2:\text{F}_2:\text{He} = 2:10:88$	1	0.73
0.918	$\text{F}_2$	0.2	0.04–0.06

in the case of LDPE with a density of  $0.926 \text{ g cm}^{-3}$ . Therefore, the results on LDPE with a density of  $0.918 \text{ g cm}^{-3}$  are not discussed in this paper. Details can be found in the authors' recent publication.<sup>21</sup>

There are two possible explanations for the formation of the  $\text{C=O}$  groups:

1. the oxyfluorination of  $-\text{CH}_3$  groups (ie reaction between  $-\text{CH}_3$  groups,  $\text{O}_2$  and  $\text{F}_2$ ); or
2. scissions of the main polymer chain.

To evaluate the amount  $N_{\text{C=O}}$  of  $\text{C=O}$ -containing groups per monomer unit, the method described in reference 28 was applied and the results of  $N_{\text{C=O}}$  measurements are shown in the Table 1. Even a small concentration of oxygen in the fluorinating mixtures can promote the formation of  $\text{C=O}$ -containing groups in LDPE significantly. A similar argument was provided by Lagow *et al.*<sup>2</sup>

To evaluate the concentration of  $-\text{CH}_3$  groups in LDPE (density  $0.918 \text{ g cm}^{-3}$ ), the IR method described in reference 32 was applied. The measured amount of  $-\text{CH}_3$  groups per 1000 carbon atoms was equal to 24.2. It was evident that even 0.4% of the oxygen in a fluorinating mixture would result in a chain scission because the concentration of  $-\text{CH}_3$  groups was far too low to explain the amount of  $\text{C=O}$  groups which were formed. It is therefore self-evident to conclude from the results discussed above that the presence of oxygen during surface fluorination can have a significant effect via chain scission upon the final attributes of a fluorinated surface layer such as its barrier properties. Moreover, with regard to the surface fluorination of polyethylene, it can be concluded that the presence of oxygen in a fluorinating gas mixture has a strongly negative influence upon the resulting

barrier properties of surface-treated substrate material.

## The relationship between fluorination and chemical composition – IR study – Summary

- (a) Fluorination results in a replacement of hydrogen atoms by fluorine atoms, but the fluorination inside the fluorinated layer is not complete. Also a set of minor groups may be formed. The presence of oxygen (even in trace amounts,  $\sim 0.1$  volume %) results in the formation of  $\text{C=O}$ -containing groups which can be hydrolysed through the activity of moisture. Those groups are hydrolysed through the action of moisture into  $-\text{COOH}$  groups.
- (b) The presence of oxygen contaminants at levels as low as 0.5% results in the formation of remarkable amounts of  $\text{C=O}$ -containing groups and leads to chain scission.

## The kinetics of formation of long-life radicals

A LDPE with a density of  $0.918 \text{ g cm}^{-3}$  was used in the ESR study on the formation and decay of radical species during surface fluorination of polyethylene, as reported here. The treatment reaction was carried out inside a dedicated quartz vessel with an internal diameter of 0.5cm and length of 20cm using oxygen-free fluorine at the temperature of liquid nitrogen ( $T = 77\text{K}$ ). The quartz reaction vessel was coated with PTFE to minimise the amount of  $\text{RO}_2^*$  radicals formed by the undesired side reactions of the polymer with, for example, surface-adsorbed oxygen, and in order to inhibit the reaction of fluorine with the quartz surface. A 30mg sample of LDPE in fibrous form was then placed in the quartz vessel. The vessel was then evacuated, placed inside the resonator of the ESR spectrometer, cooled to a constant temperature of 77K, and filled with fluorine to a pressure of 0.12 bar.

The ESR spectra were then monitored as fluorination proceeded. The spectra revealed the instantaneous formation of both fluoroalkyl and peroxy radicals, thus clearly indicating that a PTFE coating was not particularly effective in preventing the contamination of the reaction vessel from oxygen and oxygen-containing species.

The kinetics relating to the accumulation of radicals are shown in Figure 10. Radical formation commences immediately following the entry of fluorine into the

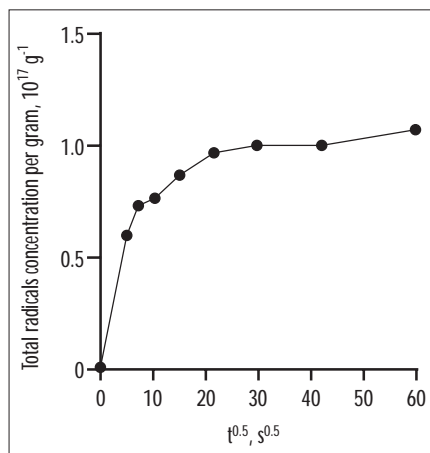


Figure 10: Total radical concentration in a fluorinated sample versus the square root of the time of fluorination as measured *in situ* at  $T = 77K$ . LDPE density =  $0.918g\ cm^{-3}$

reaction vessel and it is clearly evident that even at the temperature of liquid nitrogen, the rate of fluorination is not insignificant. In the actual experiments the concentration of the radicals soon reached a maximum concentration of around  $10^{17}$  radicals per 1g of the total sample weight after which no further radical formation took place.

It is important to note that the above-mentioned radical concentration is an average concentration which included the fluorinated and non-fluorinated parts of the sample. ESR spectra are shown in Figure 11. Spectrum 1 was measured 20 minutes after ingress of fluorine (fluorine pressure  $\sim 0.095$  bar and treatment temperature  $77K$ ). Spectra 2 and 3 corresponded to the same sample evacuated after fluorination and oxidised by atmospheric air and measured at  $77K$  and  $293K$  correspondingly. In order to identify the radicals formed during surface fluorination, samples of LDPE (density of  $0.918g\ cm^{-3}$ ), PVF, PVDF and PTFE were each gamma-irradiated and their ESR spectra measured. The ESR spectrum 4 in Figure 11 is the spectrum of gamma-irradiated virgin LDPE irradiated under conditions where only secondary alkyl  $-CH_2-CH^{\bullet}-CH_2-$  radicals were formed while the formation of allyl  $-CH_2-CH^{\bullet}-CH=CH-CH_2-$  radicals remained negligible.<sup>33</sup>

Gamma-irradiation of the fluorinated polymers such as PVF, PVDF and PTFE resulted in formation of species such as  $-CH_2-CF^{\bullet}-CH_2-$ ,  $-CF_2-CF^{\bullet}-CH_2-$  and  $-CF_2-CF^{\bullet}-CF_2-$ . Due to the presence of F-atoms, the ESR spectra of these radicals were characterised by a very large superfine splitting. As a result, the total width of the related ESR spectra – around  $\sim 35mT$  – was much greater than

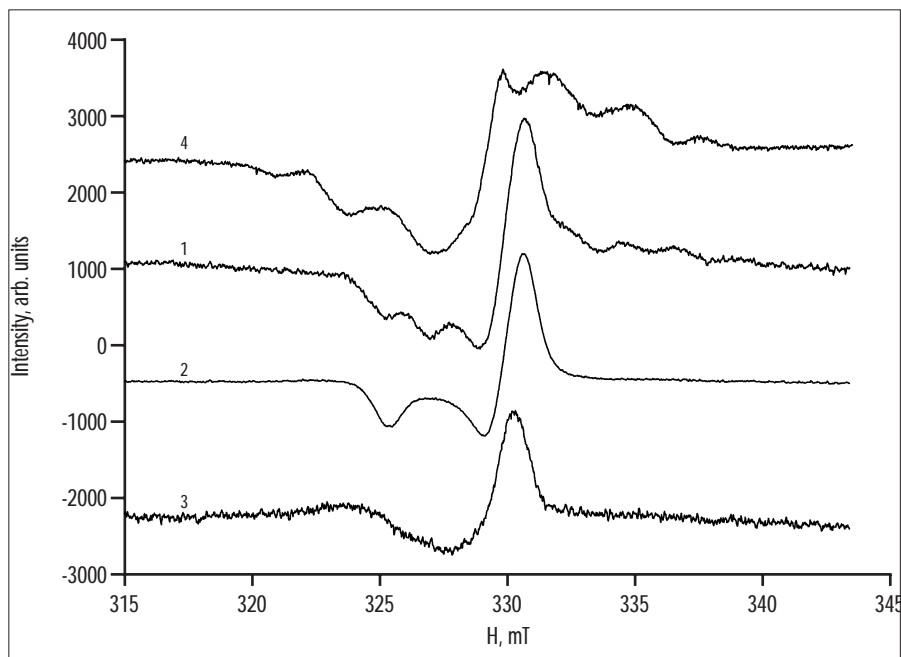


Figure 11: 1: ESR spectrum of a LDPE sample in the form of ‘cotton wool’ as measured 20 minutes after the insertion of fluorine into the reaction vessel. The reaction was carried out at  $T = 77\ K$ ; 2 and 3: spectra of the same sample which was evacuated after fluorination and oxidised. Curve 4: spectrum of gamma-irradiated (in vacuum at  $T = 77K$ ) LDPE. Spectra 1, 2 and 4 were measured at  $77K$ , spectrum 3 at  $293K$ . The spectra were corrected with respect to the absorption of the sample before fluorination

that associated with analogue fluorine-free alkyl radicals.

Spectrum 1 in Figure 11 was measured 20 minutes after the insertion of fluorine into the reactor ( $p_F = 0.095$  bar). The resulting spectrum is a combination of absorptions originating from the peroxy species  $RO_2^{\bullet}$  and another radical which resembled the allyl  $-CH_2-CH^{\bullet}-CH=CH-CH_2-$  radical<sup>33</sup> rather than the secondary alkyl radical  $-CH_2-CH^{\bullet}-CH_2-$  (see reference 4, Figure 11). The super-fine splitting is too small for the fluorine-containing component formed in the irradiated PVF, PVDF or PTFE. Therefore, it is likely that during the initial stages of fluorination of the technical polyethylene, allyl radicals are formed and that these radicals initiate the subsequent fluorination of the polymer. This indicates that the fluorination starts with the abstraction of H-atoms bonded in allyl positions, and explains the fact that HDPE reacts faster than LDPE because more double bonds were found in HDPE than in LDPE. However, at  $T = 77K$ , no further reactions took place. This behaviour may be due to the existence of an activation energy barrier associated with further chain propagation and hence very low temperatures would, to a great extent, lower the rate constants of the subsequent chain reactions.

Spectra 2 and 3 in Figure 11 are the spectra of the same sample measured at  $77K$  and  $293K$  respectively. It is evident

from the spectra, which shows typical asymmetric singlet absorptions, that all the initially formed radicals are transformed into peroxy  $RO_2^{\bullet}$  radicals.

Similar results were obtained for flat LDPE films treated with undiluted fluorine for  $t = 100$  minutes at  $T = 293K$  and  $0.072$  bar fluorine partial pressure (see Figure 12). The asymmetric singlet in the ESR spectrum ( $g_{\perp} = 2.0022$ ,  $g_{\parallel} = 2.0356$ ) corresponds to the  $RO_2^{\bullet}$  radical. Remarkably, the ESR spectra recorded at  $77K$  and at room temperature are virtually coincident.

The latter result can be readily explained with the formation of secondary or ‘middle’ peroxy  $RO_2^{\bullet}$  radicals such as  $\sim CHOO^{\bullet}$  or  $\sim CFOO^{\bullet}$ , and terminal species such as  $\sim CH_2OO^{\bullet}$  or  $\sim CHFOO^{\bullet}$  or  $\sim CF_2OO^{\bullet}$ . The spectra of ‘middle’ and ‘end’ radicals measured at  $77K$  should be similar because of the ‘frozen’ (restricted) rotation around the polymer chain, which results in similar g-factor components were thus also similar (see Figures 11 and 12). When measured at room temperature, the spectra of ‘middle’ and ‘end’ radicals should differ from each other. The unrestricted rotation of the ‘end’  $RO_2^{\bullet}$  radical around the C–O bond and the axis of the polymer chain results in an averaging of the anisotropy of the g-factor and hence results in a totally symmetric singlet spectrum. As the rotation of the ‘middle’  $RO_2^{\bullet}$  radical around a C–O bond and

axis of a polymer chain is restricted, the g-factor is averaged only partially, and the spectrum becomes an asymmetric singlet. The detailed examination of the spectrum measured at room temperature leads to the conclusion that the majority of the radicals are 'middle' radicals. This indicates that disruptions of the polymer chain in LDPE treated under conditions similar to that of industrial 'off-line' processes are practically absent. The same experiment (insertion of fluorine into the reaction vessel at  $T = 77\text{K}$ ) was carried out at a lower fluorine pressure (ie  $\sim 0.011$  bar), and again a mixture of peroxy and alkyl/allyl radicals were detected. Subsequent heating of the reaction vessel to room temperature resulted in the termination of the peroxy radicals in less than 15 minutes. This can be regarded as confirmation that those peroxy radicals had a carbon-hydrogen character (ie  $-\text{CH}_2-\text{COO}^{\bullet}-\text{CH}_2-$  or similar) because fluorocarbon peroxy radicals are known to have significantly greater lifetimes.<sup>34</sup>

### Kinetics of the termination of long-lifetime radicals

#### LDPE density $0.918\text{g cm}^{-3}$

Polymer films were fluorinated at  $T = 293\text{K}$  and stored in appropriate glass vials at liquid nitrogen temperature. Subsequently the ESR spectra were measured. The sample was then allowed to heat up to room temperature ( $T = 291\text{K}$ ). Then the ESR spectra were measured again at  $77\text{K}$  and compared with spectra obtained at low temperature measurements. In all measurements, both peroxy  $\text{RO}_2^{\bullet}$  and perfluoroalkyl radicals were detected. However, the majority of the radicals were found to be of the peroxy type. The experimental conditions are summarised in Table 2.

The kinetics of radical termination at  $T = 293\text{K}$  are shown in Figure 11. It should be noted that a radical half-life  $t_{1/2}$  (ie the time interval required for a decrease in radical concentration by a factor of 2) was close to between five and six hours.

#### LDPE density $0.926\text{g cm}^{-3}$

The procedure for the treatment and testing of polymer films is described above and the experimental conditions are summarised in Table 3. The kinetics of radical termination at  $T = 293\text{K}$  are shown in Figure 11. It should be noted that the half-life for radical termination  $t_{1/2}$  was close to between four and four and a half hours.

It is evident that the direct fluorination of LDPE generated a high concentration of

long-lifetime radicals. In the experiments described here radical concentrations between  $3 \cdot 10^{19}$  to  $5 \cdot 10^{19}$  radicals per  $\text{cm}^3$  of fluorinated polymer were determined. This means that roughly  $\sim 0.3\%$  of the monomeric units of fluorinated LDPE contained radicals – mainly peroxy  $\text{RO}_2^{\bullet}$  radicals. The average half-life-time of these radicals was four to six hours at room temperature. A decrease of both fluorine partial pressure and treatment time resulted in a small decline in concentration of the long-life-time radicals.

Two types of peroxy  $\text{RO}_2^{\bullet}$  radicals can be formed: in the middle of a chain ('middle radicals',  $\sim\text{CHO}_2^{\bullet}\sim$  or  $\sim\text{CFO}_2^{\bullet}\sim$ ), and at the end of a chain ('end radicals',  $\sim\text{CH}_2\text{O}_2^{\bullet}$  or  $\sim\text{CHFO}_2^{\bullet}$  or  $\sim\text{CF}_2\text{O}_2^{\bullet}$ ). To distinguish 'middle' and 'end' radicals, the following experiment was carried out. A LDPE sample was treated with a  $\text{F}_2/\text{O}_2$  mixture to form  $\text{RO}_2^{\bullet}$  radicals. The ESR spectra of the treated LDPE samples were measured at a temperature of  $77\text{K}$  and  $293\text{K}$ . It was found that the spectra were similar because of restricted rotation and the g-

**Table 2: Concentration of radicals in LDPE treated under different conditions**

Sample no	Fluorine pressure (Torr)	Treatment time (minutes)	Maximum concentration of radicals per $\text{cm}^3$ of fluorinated layer (radicals $\text{cm}^{-3}$ )	Percentage of peroxy $\text{RO}_2^{\bullet}$ radicals (%)
LD2-E1	73.5	15	$5.2 \cdot 10^{19}$	80–90
LD2-E2	73.5	30	$2.8 \cdot 10^{19}$	80–90
LD2-E3	73.5	60	$2.6 \cdot 10^{19}$	80–90

**Table 3: Concentration of radicals in LDPE treated under different conditions**

Sample no	Fluorine pressure (Torr)	Treatment time (minutes)	Maximum concentration of radicals per $\text{cm}^3$ of fluorinated layer (radicals $\text{cm}^{-3}$ )	Percentage of peroxy $\text{RO}_2^{\bullet}$ radicals (%)
LD1-E2	147	85	$4.0 \cdot 10^{19}$	80
LD1-E3	88.2	85	$3.0 \cdot 10^{19}$	85
LD1-E4	147	45	$3.3 \cdot 10^{19}$	80
LD1-E5	88.2	45	$2.5 \cdot 10^{19}$	95
LD1-E6	147	15	$3.7 \cdot 10^{19}$	95–100

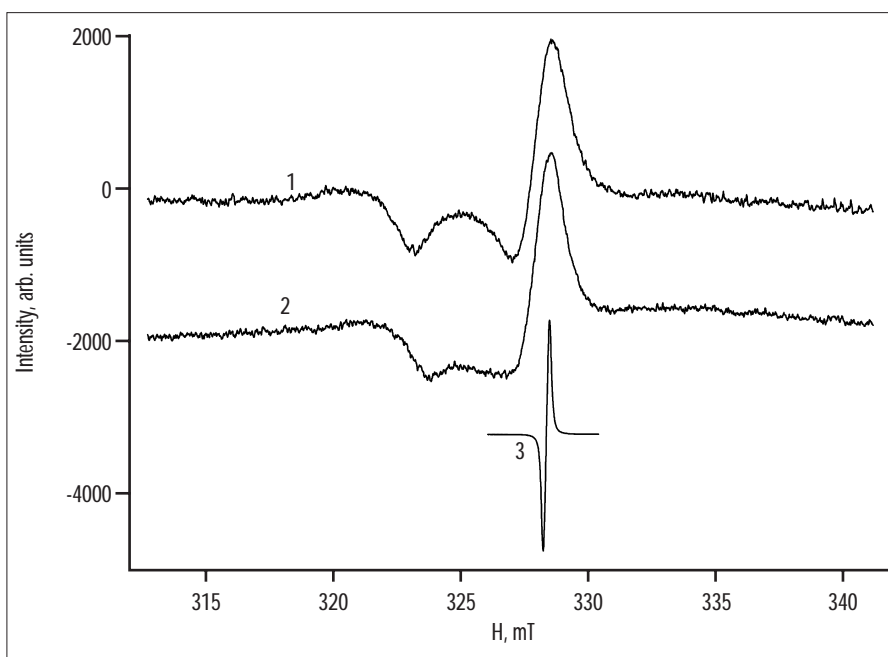


Figure 12: ESR spectra of LDPE samples in the form of a flat film fluorinated at room temperature. Treatment conditions: undiluted fluorine,  $p_F = 0.072$  bar, fluorination time  $t = 100$  minutes at  $T = 293\text{K}$ . Spectra 1 and 2 were measured at  $77$  and  $293\text{K}$  respectively. 3: DPPH spectrum ( $g = 2.0036$ ). The spectra were corrected with respect to the absorption of the sample before fluorination

**Table 4: Measured concentration of double bonds and CH<sub>3</sub> groups in virgin LDPE and HDPE**

Polymer	Relative concentration of double bonds (moles of double bonds per moles of the main polymer unit)				Total concentration of double bonds	Amount of CH <sub>3</sub> groups per 1000 C atoms
	Trans-vinylene -CH=CH-	Vinyl -CH=CH <sub>2</sub>	Vinylidene R <sub>1</sub> R <sub>2</sub> C=CH <sub>2</sub>	Conjugated diene -CH=CH-H=CH-		
LDPE density 0.918g cm <sup>-3</sup>	1.1·10 <sup>-4</sup>	1.1·10 <sup>-4</sup>	6.5·10 <sup>-4</sup>	0	0.87·10 <sup>-3</sup>	24.2
HDPE no 1	0.93·10 <sup>-4</sup>	1.9·10 <sup>-3</sup>	1.4·10 <sup>-4</sup>	1.9·10 <sup>-4</sup>	2.2·10 <sup>-3</sup>	3.7
HDPE no 2	0.64·10 <sup>-4</sup>	1.9·10 <sup>-3</sup>	0.37·10 <sup>-4</sup>	2.3·10 <sup>-4</sup>	2.2·10 <sup>-3</sup>	3.9
HDPE no 3	1.2·10 <sup>-4</sup>	2.4·10 <sup>-3</sup>	0.87·10 <sup>-4</sup>	2.6·10 <sup>-4</sup>	2.9·10 <sup>-3</sup>	3.9
HDPE no 4	0.67·10 <sup>-4</sup>	2.5·10 <sup>-3</sup>	0.56·10 <sup>-4</sup>	2.6·10 <sup>-4</sup>	2.9·10 <sup>-3</sup>	2.5
HDPE No.5	0.52·10 <sup>-4</sup>	1.4·10 <sup>-3</sup>	0.26·10 <sup>-4</sup>	1.6·10 <sup>-4</sup>	1.6·10 <sup>-3</sup>	4.1

factor components were also found to be similar (ie  $g_{||} = 2.033$  and  $g_{\perp} = 2.001$ ) (see Figure 12). When measured at room temperature, the spectra of the 'middle'  $\sim\text{CF}_2\text{-CF}(\text{OO}^*)\text{-CF}_2\sim$  and the 'end'  $\sim\text{CF}_2\text{-CF}_2\text{-OO}^*$  radicals differed from each other. The reason is that unlimited rotation of the 'end'  $\text{RO}_2^*$  radical around the C-O bond and the axis of the polymer chain resulted in an averaging of the anisotropy of the g-factor and hence resulted in a totally symmetric singlet spectrum. On the other hand, rotation of the 'middle'  $\text{RO}_2^*$  radical around a C-O bond and the axis of the polymer chain would be restricted, the g-factor would thus be averaged only partially, and the spectrum would be an asymmetric singlet. Through examination of the spectrum measured at room temperature (see Figure 12, asymmetric singlet), it is possible to form the conclusion that the majority of the radicals were 'middle' radicals and that disruptions of the polymer chain within this polymer were also practically absent.

### The kinetics of elementary reactions – Summary

- The process of LDPE fluorination is a radical process.
- Initiation of the reaction takes place via the reaction of molecular fluorine with C-H bonds and not via the dissociation of molecular fluorine.
- Both peroxy long-lifetime  $\text{RO}_2^*$  and fluororadicals are formed within the fluorinated layer in large concentrations. The amount of peroxy radicals exceeds the amount of fluororadicals.
- Termination time (ie the time required for a reduction in the amount of radicals by a factor of 2) of long-lifetime radicals for LDPE is relatively large and is around four to six hours. Hence additional modification of the polymer surface can be arranged via grafting of monomers containing double bonds.

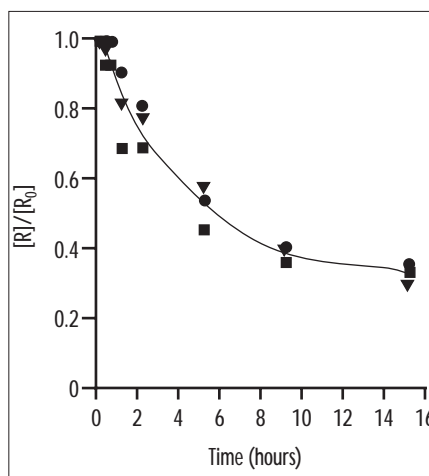


Figure 13: Ratio  $[R]/[R_0]$  ( $[R]$ -concentration of radicals at time  $t$ ,  $[R_0]$ -concentration of radicals 12 minutes after completion of fluorination) versus storage time  $t$  in the case of LDPE of a density of  $0.918\text{g cm}^{-3}$ . Circles: LD2-E1 (see Table 3); squares: LD2-E2; triangles: LD2-E3

- The amount of scissions in LDPE treated under industrial conditions is negligible.

### Preliminary schematic of the elementary reactions

As mentioned above, the fluorination of LDPE can be regarded as a radical process. In addition, another important conclusion concerning the initiation stage of the fluorination process can be made. The initiation stage (ie the formation of carbon-hydrogen radicals) proceeds even at liquid nitrogen temperatures (see above). This implies that the initial reaction step proceeds with almost zero activation energy. The commonly proposed initiation reaction involving the dissociation of molecular fluorine  $\text{F}_2 \rightarrow \text{F}^* + \text{F}^*$  – a reaction which is endothermic by  $159\text{kJ/mol}$  – does not fulfil this important requirement. However, there are a number of exothermic reactions involving molecular fluorine which are more appropriate candidates for the initial reaction step.

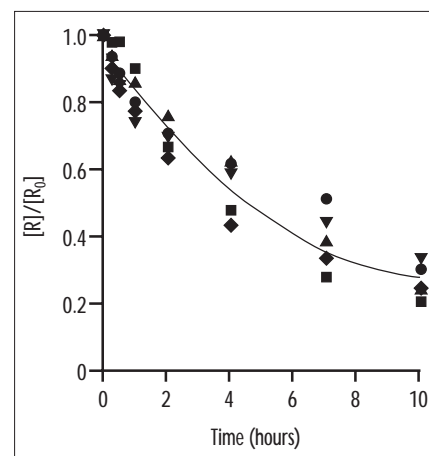
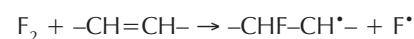
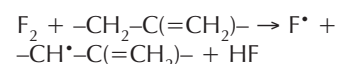
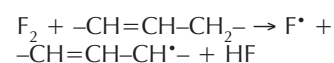
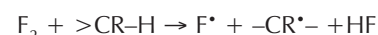


Figure 14: Ratio  $[R]/[R_0]$  ( $[R]$ -concentration of radicals at time  $t$ ,  $[R_0]$ -concentration of radicals 12 minutes after completion of fluorination) versus storage time  $t$  in the case of LDPE density of  $0.926\text{g cm}^{-3}$ . Circles: LD1-E2 (see Table 4); horizontal squares: LD1-E3; triangles corner up: LD1-E4, triangles corner down: LD1-E5; diamonds: LDF1-E6

Among these reactions, the slightly exothermic branching reaction between  $\text{F}_2$  and  $-\text{CH}_2-$  is likely to predominate:  $\text{F}_2 + -\text{CH}_2- \rightarrow \text{F}^* + -\text{CH}^* + \text{HF}$ .

The actual presence of a high concentration of  $-\text{CH}_2-$  groups favours the  $\text{F}_2 + -\text{CH}_2-$  reaction over other theoretically possible initial step reactions such as the reaction of  $\text{F}_2$  with tertiary C-H groups or double C=C bonds. (Transvinylene, vinyl, vinylidene and conjugated diene bonds are always present in all the polyethylenes as impurities; see below):

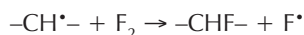
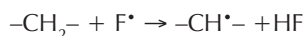


It is necessary to emphasise that, for example, the reaction between  $\text{F}_2$  and double bonds, tertiary bonded hydrogen or weakly bonded allylic hydrogen may play an important role in industrial or

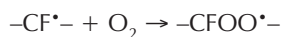
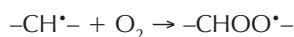
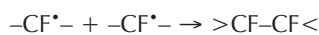
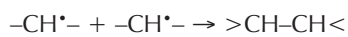
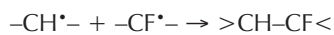
pre-processed polyethylene in which the molecular structures deviate more or less significantly from the very regular  $-\text{CH}_2-\text{CH}_2-$  structure of ideal polyethylene.

FTIR spectroscopy was used to determine the concentration of C=C double bonds and  $-\text{CH}_3$  groups. ( $-\text{CH}_3$  groups which will hardly react with  $\text{F}_2$  because of the very strong C-H bonds were in particular used as for polymer branching and therefore as an initiator for the presence of tertiary C-H bonds.) The extinction coefficients were taken from a number of sources.<sup>32,35,36</sup> The data obtained are shown in Table 4. Approximately 0.1% of the polymer units of LDPE and between 0.2% and 0.3% of the polymer units of HDPE had double bonds and the concentration of the  $-\text{CH}_3$  groups was around 2.4% for LDPE and between 0.3% to 0.4% for HDPE with respect to the amount of carbon atoms. Usually such a concentration of initiators is enough to start a chain process. A similar initiation mechanism has been proposed in earlier publications by Kharitonov and Moskvina.<sup>28,30,37</sup>

(f) The chain propagation reactions may have an activation energy but the following exothermic processes can be proposed:



(g) The reactions shown below are likely candidates for a chain termination reaction. Some of the reactions are highly exothermic and may cause C-C bond scission.



The absence of 'end' peroxy radicals indicates that the chain scission does not occur.

## Conclusions

1. The fluorination of polyethylene proceeds via a branched chain-radical mechanism following an induction period.
2. Initiation of the reaction likely takes place via the reaction of molecular fluorine with C-H bonds and not via

the dissociation of molecular fluorine.

3. Fluorination results in a replacement of hydrogen atoms with fluorine atoms, but the fluorination inside the fluorinated layer is not complete.
4. The fluorination of polyethylenes is a diffusion-controlled process. This indicates that the rate of formation of a fluorinated layer is limited by the rate of penetration of fluorine through the fluorinated polymer layer into the untreated layer. The fluorinated and untreated layers are separated by a very thin transient boundary layer where the majority of the chemical reaction takes place.
5. The rate of formation of a fluorinated layer increases with fluorine partial pressure and temperature and was not observed to be affected by the presence of He and/or  $\text{N}_2$  in the fluorinating mixture.
6. There is practically no correlation of the fluorination rate with the actual density of the HDPE or with the presence of additives such as carbon black.
7. The rate of fluorination of HDPE significantly exceeds that of LDPE.
8. The fluorination rate of PVF is almost identical to the fluorination rate of LDPE.
9. PVDF cannot be fluorinated even at temperatures as high as 430K and/or under UV irradiation.
10. The presence of oxygen (even in trace amounts, ~0.1-0.2 volume %) results in the formation of C=O-containing groups and leads to chain scission. Those groups are hydrolysed under the action of moisture into  $-\text{COOH}$  groups.
11. Long-lifetime peroxy  $\text{RO}_2 \cdot$  and fluororadicals are formed inside the fluorinated layer in large concentrations. The amount of peroxy radicals exceeds that of fluororadicals. The termination time (ie the time necessary for the amount of radicals to decrease by a factor of 2) of the long-lifetime radicals is around four to six hours.
12. It is mainly middle peroxy radicals that are formed under treatment conditions close to those used in industrial processes. Therefore, the amount of scissions in LDPE treated under industrial conditions is negligible.

## References

1. Kharitonov A P, 'Practical applications of the direct fluorination of

polymers', *J Fluorine Chem*, **103**, 123, 2000

2. Lagow R J and J L Margrave, 'Direct fluorination: a 'new' approach to fluorine chemistry', *Progr in Inorg Chem*, **26**, 162, 1979
3. Jagur-Grodzinski J, 'Modification of polymers under heterogeneous conditions', *Progr in Polymer Sci*, **17**, 361, 1992
4. Anand M, J P Hobbs and I J Brass, 'Surface fluorination of polymers', *Organofluorine Chemistry: Principles and Commercial Applications*, (eds) R E Banks, B E Smart and J C Tatlow, 469-81, Plenum Press, New York, 1994
5. Lagow R J and J L Margrave, 'Letters to the Editor', *J Polymer Sci Polymer*, **12**, 177, 1974
6. Moorehead A and L Margrave, 2nd International Conference, 'Fluorine in coatings', Conference paper no 15, Salford, England, 28th to 30th September 1994
7. Hara N, H Fukumoto and M Watanabe, 'In-situ kinetic study on direct fluorination of thin polyethylene films with QCM', *Bull Chem Soc Jpn*, **68**, 1232, 1995
8. Corbin G A, R E Cohen and R F Baddour, 'Kinetics of polymer surface fluorination: Elemental and plasma-enhanced reactions', *Polymer*, **23**, 1546, 1982
9. Millard M, J Burns and B Sachdev, 'Mild direct fluorination of polymers studied by x-ray photoelectron spectroscopy', *Proceedings of the International Symposium (ACS)*, **2**, 773, London, 1983
10. Schonhorn H and R H Hansen, 'Surface treatment of polymers. II. Effectiveness of fluorination as a surface treatment for polyethylene', *J Appl Polymer Sci*, **12**, 1231, 1968
11. R D Sanderson, F J du Toit, P A B Carstens, J B Wagener, 'Fluorination rates of polyolefins as a function of structure and gas atmosphere', *J of Thermal Analysis*, **41**, 563, 1994
12. Shinohara H, M Iwasaki, S Tsujimura, K Watanabe and S Okazaki, 'Fluorination of polyhydrofluoroethylenes. I. Direct fluorination of poly(vinyl fluoride) film', *J Polymer Sci A-1*, **10**, 2129, 1972
13. Scherer G G, P Pfluger, H Braun, J Klein and H Widdecke, 'Elemental fluorination of poly(vinylidene fluoride)', *Macromol Chem Rapid Commun*, **5**, 611, 1984
14. Blackwell C S, P J Degen and F D Osterholtz, 'Internal reflectance spectroscopy of reacted surfaces: Fluorinated polyethylene and polypropylene', *Appl Spectr*, **32**, 480, 1978

15. Nazarov V G, V P Stolyarov, L A Evlampieva and A F Fokin, 'Heterogeneous fluorination of polymers', *Doklady Akademii Nauk*, **350**, 639, 1996 (in Russian)
16. Florin R E, 'Electron-spin resonance-spectra of polymers during fluorination', *J Fluorine Chem*, **14**, 253, 1979
17. Florin R E and L A Wall, 'Radicals detected by electron spin resonance during fluorination of polymers', *J Chem Phys*, **57**, 1791, 1972
18. Kuzina S I, A P Kharitonov, Yu L Moskvina and A I Mikhailov, 'Formation of free radicals in the low-temperature fluorination of polymers', *Russ Chem Bull*, **45**, 1623, 1996
19. Taege R, G Ferrier and A P Kharitonov, Proceedings from the 16th European Symposium on Fluorine Chemistry, A34, Durham, UK, 16th to 21st July 2000
20. Kharitonov A P, N P Piven, R Taege and G Ferrier, Proceedings from the first international Siberian Workshop Intersibfluorine 2003 (Advanced Inorganic Fluorides), 253, Novosibirsk, Russia, 2nd to 4th April 2003
21. Kharitonov A P, N P Piven, R Taege and G Ferrier, Proceedings from the 5th international Fluorine in Coatings conference, Paper no 8, Orlando, Florida, USA, 21st to 22nd January 2003
22. Shamir J and J Binenboym, 'Photochemical synthesis of dioxygenyl salts', *Inorganica Chimica Acta*, **2**, 37, 1968
23. Kharitonov A P, Yu L Moskvina and G A Kolpakov, 'Application of the interference spectroscopy method to study the kinetics of chemical reactions in optically transparent films', *Polymer Science USSR*, **27**, 739, 1985
24. Kharitonov A P, Yu L Moskvina and G A Kolpakov, 'The direct fluorination of polyethylene terephthalate films', *Sov J Chem Phys*, **4**, 877, 1987
25. Kharitonov A P, Yu L Moskvina, L N Kharitonova, M N Tulskaia and A A Kotenko, 'An investigation into the direct fluorination kinetics of polymeric membranes', *Mendeleev Communications*, **N3**, 91, 1994
26. Kharitonov A P, Yu L Moskvina, L N Kharitonova, A A Kotenko and M N Tulskaia, 'Kinetics of gas-phase fluorination of homogeneous films and composite membranes based on polycarbonate siloxane and block-copolymer of polysulfone and polybutadiene', *Kinetics and Catalysis*, **35**, 792, 1994
27. Kharitonov A P, Yu L Moskvina, L N Kharitonova, A A Kotenko and M N Tulskaia, 'Use of interference methods for study of the fluorination kinetics of homogeneous and composite polymeric membranes', *Polymer Science*, **B37**, 307, 1995
28. Kharitonov A P and Yu L Moskvina, 'Direct fluorination of polystyrene films', *J Fluorine Chem*, **91**, 87, 1998
29. Kharitonov A P, Yu L Moskvina, V V Teplyakov and J D Le Roux, 'Direct fluorination of poly(vinyl trimethylsilane) and poly(phenylene oxide)', *J Fluorine Chem*, **93**, 129, 1999
30. Kharitonov A P and Yu L Moskvina, Proceedings from the 2nd international Fluorine in Coatings conference, Paper no 13, Salford, England, 28th to 30th September 1994
31. Socrates G, *Infrared Characteristic Group Frequencies*, 34–51, 62–7, 80–118, 155–60, (2nd edition), John Wiley & Sons, Chichester, NY, Brisbane, Toronto, 1994, ISBN 0 471 94230 8
32. Willbourn A H, *J Polymer Science*, **34**, 569, 1959
33. Milinchuk V K, E R Klinshpont and S Ya Pshejckii, 'Chemistry' edition, Makroradikaly, Moscow, 1980 (in Russian)
34. Kolpakov G A, S I Kuzina, A P Kharitonov, Yu L Moskvina and A I Mikhailov, 'Free radical accumulation during direct fluorination of polystyrene', *Sov J Chem Phys*, **9**, 2283, 1992
35. Dole M, D C Milner and T F Williams, 'Irradiation of polyethylene. II. Kinetics of unsaturation effects', *J Amer Chem Soc*, **80**, 1580, 1958
36. Dekhant J, R Danz, V Kimmer and R Schmolke, *Ultrarotspektroskopische Untersuchungen an Polymeren*, Chapter 5.2, Akademie-Verlag, Berlin, 1972 (in German)
37. Kharitonov A P and Yu L Moskvina, 'Kinetics of the direct gas phase fluorination and the gaspermeability of polystyrene films', *Chemical Physics Reports*, **13**, 818, 1994 (formerly the *Sov J Chem Phys*)

